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AFM-based approach to establish structure/property type correlations for polymeric functional materials

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The development of polymer-based functional materials with controlled structure and properties is closely associated with different physical, chemical and material science problems. Fundamental research of polymers structure and their functional properties is needed for the solution of those problems.

Now there are a variety of methods for studying polymeric materials [1-3]. Each of the methods with a range of advantages and drawbacks has a specific application. Since it is known that mechanical and physical properties of polymer-based materials not only depend on their chemical nature but also strongly correlate with their surface structure, the study of this effect is an important task.

For example, in the case of gas separation processes, a non-porous polymeric membrane surface has significant contribution to not only mechanical, but also gas transmission properties. It is due to the fact that first stages in gas separation are deposition of permeating gases on a membrane surface and their absorption. The rougher a membrane surface, the larger will be its actual area, and with the growth of this area, the separation speed also increases, that is, permeable properties are improved.

A polymeric surface can be assessed by atomic force microscopy (AFM). This method is suitable for such study, not only because of high lateral and vertical resolutions, but also its ability of gaining quantitative three-dimensional information about topography without destruction of a soft polymer surface. However, AFM imaging results alone are not sufficient to assess the impact of polymeric morphological features on their properties. For example, to establish the correlation of polymer surface features with its wettable and mechanical properties, it is necessary to use the approach based on AFM combined with wettability measurements and mechanical testing.

In this work, this approach was used to study a range of polymeric films based on polysulfone (PSU), cellulose triacetate (CTA) and polyvinyl alcohol (PVA).

PSU, CTA and PVA flat shits were obtained by corresponding polymer solution casting using automatic coating machine MemcastPlus (Porometr, Belgium) onto inert support followed by solvent evaporation under equilibrium conditions. Solutions of polymers were prepared in the following proportions: 7.5 % PSU in tetrahydrofuran (THF), 1.5 % CTA in glacial acetic acid, 3 % PVA in water. After the polymer films formation they were easily peeled off the support and desiccated under vacuum for 24 hours. Each of the polymers was cast on three glass substrates.

Borosilicate glass was chosen as an inert support, due to its chemical, thermal and mechanical stability. Before use the glass was chemically treated in order to obtain certain surface roughness. Glass support 1 was exposed in the 5 % hydrofluoric acid solution for 10 min, glass support 2 was exposed in the 15 % hydrofluoric acid solution containing 50 % ammonium fluoride for 5 min and glass support 3 was exposed under etching paste containing 30 % HF, 30 % NH_4F and 15 % $BaSO_4$ for 5 min. After etching glass supports were rinsed thoroughly with distilled water in ultrasound bath for 10 min.

The glass supports surface and their roughness were studied by a scanning probe microscope SPM-9700 (Shimadzu, Japan). AFM scanning was performed using a contact mode by silicon nitride cantilevers OMCL-TR800PSA (Olympus, Japan) with a stiffness coefficient of 0.57 N/m and a typical tip radius of no more than 15 nm (guaranteed - no more than 20 nm), a tip height was 29 microns. The experiments were carried out under ambient conditions. Automatic correction of linear noise was applied during scanning. For checking purposes reproducibility, AFM scanning was carried out on different sites of the studied surfaces. After AFM scanning, an arithmetic average

roughness height (R_a) and a mean roughness depth (R_z) were obtained. A base length was 10 μm (Table 1). Processing of the obtained AFM images and their analysis were performed by a software SPM Manager ver. 4.02 (Shimadzu, Japan).

Table 1. The roughness parameters.

R_a, ± 0.01 nm				R_z, ± 0.02 nm			
Support	PSU	CTA	PVA	Support	PSU	CTA	PVA
6.93	1.46	2.88	5.62	39.51	47.03	54.16	37.23
34.94	54.17	54.95	50.27	126.85	260.53	272.55	205.75
137.59	175.20	170.30	173.33	543.51	688.68	710.37	752.47

The same way, the polymers surface was studied. But since polymeric materials have a loosely-coupled surface structure, AFM scanning was performed using a tapping mode by silicon vibrating cantilevers PointProbe FMR-20 (Nano World Innovative Technologies, USA) with a stiffness coefficient of 1.3 N/m and a typical tip radius of no more than 8 nm (guaranteed - no more than 12 nm), a tip height was 15 microns.

According to the AFM results, the polymers surface roughness increases with the growth of the glass supports roughness which is quite logical (Table 1). But it is noteworthy that the films surface roughness is different in the case of the glass support 1 and close in the case of the glass supports 2 and 3. This can be explained as follows. The rigid-chain properties of the studied polymers decrease in the following order: PSU, CTA, PVA. Hence, the higher intermolecular rotation freedom of a polymer, the more its surface reflects a glass support structure and its roughness. At significant values of glass supports roughness, this effect is brought to nothing.

An advancing contact angle of wetting for PSU, CTA and PVA surfaces oriented to glass supports was determent by wettability tests using diiodomethane as test liquid. An image of the drop applied to the sample surface was processed with the ImageJ software in order to calculate the advancing contact angle. According to the obtained measurements, a decrease of wetting with an increase in the surface roughness of the sample was observed for all polymers. This is explained that surfaces with significant roughness tend to be superhydrophobic and not wetted by most liquids.

Mechanical properties of the polymeric films (namely, values of a tensile strength (σ)) were determined on a universal test machine Zwick Z005 (Zwick Roell, Germany) at a pulling speed of 50 mm/min. With the PSU surface roughness growth, its tensile strength decreased from 56 to 44 MPa. This trend is supposedly associated with an increase in the macromolecules rod-like packing defectiveness of rigid-chain PSU. The opposite tendency was observed in the case of PVA. Its tensile strengths increased from 61 to 85 MPa, which is explained by the probable formation of additional intermolecular hydrogen bonding in the extended near-surface layer of this flexible-chain polymer. In contrast with PSU and PVA, CTA tensile strength didn't change (about 57 MPa), which is due to its rigid-chain properties in combination with the ability to form hydrogen bonding.

Thus, it is shown that, polymers wettable and mechanical properties can be controlled by varying their surface roughness with due regard to their chemical nature. At that, necessary correlations of a structure/property type can be established using the considered AFM-based approach.

This work was supported by the RSF (project No. 18-19-00453) and the RFBR (project No. 18-08-01356 A).

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